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The objective of our work is to harness the computational power of large parallel computers to obtain electron collision cross sections needed in modelling the chemical and physical properties of flowfields over hardbodies. Such electron collision data are very fragmentary, often not available, and difficult to measure.

We have developed a scalable implementation of our formulation of electron-molecule collisions. With these scalable algorithms we routinely achieve aggregate performance in the tens of gigaflop range on available computer system. This capability has allowed us to carry out sophisticated first-principles calculations of electron collisions with species such as N_2, O_2, CO, NO, and H_2O.

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Electron-Molecule Collisions and UV Signatures in Flowfields

Final Technical Report

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I. *Background and Objectives*

Electrons produced in the bow shock of missiles can play an important role in determining the chemical and physical properties of hypersonic flowfields. Due to non-equilibrium overshoots, electron temperatures can rise above 10,000 K in such flowfields. Furthermore, as flight velocities increase, electron number densities and collisions become more significant. However, electron collision data needed in simulations of these flowfields are very fragmentary and often not available. This is particularly true for near-threshold excitation processes where the incident electrons barely have enough energy to drive the excitation and for collisions with metastable states and with fragments such as OH.

Our strategy for obtaining these electron-collision cross section data, particularly those that are experimentally inaccessible, has been to calculate them. Calculations of electron-collision cross sections at the low energies of interest in flowfields, are also difficult. In fact, although the physical principles in low-energy electron-molecule collisions are well understood, and although several methods have been developed for numerical studies of these collisions, progress in their application has been very limited. What is required is not just a method and algorithm by which these cross sections can be calculated in principle, but an implementation that makes relevant problems feasible. The thrust of our effort has hence been to develop innovative scalable implementations of our formulation of electron-molecule collisions[1,2] with which we could harness the computational power of larger parallel computers to obtain electron-collision data needed in modeling flows.

II. *Summary of Progress and Accomplishments*

At the low energies of interest in these flowfields, an accurate quantum-mechanical treatment of the full 3(N+1)-dimensional space of the Schrödinger's equation that governs the collision of an electron with an N-electron molecule is necessary; low-order approximations, such as the Born

approximation, are not applicable. Furthermore, because direct numerical integration of Schrödinger's equation in this 3(N+1)-dimensional space is not practical, most recent studies rely on the use of variational approximations to obtain the scattering amplitudes for these collisions. Our studies are based on the Schwinger multichannel (SMC) method,[1] an extension of Schwinger's variational principle. This SMC variational principle was specifically developed for applications to low-energy electron-molecule collisions and possesses compelling computational advantages. However, these come at the cost of evaluating a Green's operator whose matrix representation is obtainable only by numerical quadrature of a class of integrals.[2] Indeed, evaluating and transforming the data for this quadrature is the principal computational task in applications. Not surprisingly, this task had been a bottleneck and hindrance to wider applications of the SMC on sequential computers such as the Cray Y-MP.

We have successfully developed efficient, scalable algorithms for carrying out the main computational tasks in these calculations on large distributed-memory parallel computers consisting of several hundreds of interconnected microprocessors. Our strategy for "parallelization" of these two main tasks – namely, evaluation of a large number (typically 10^{12} to 10^{15}) of elementary integrals and their subsequent transformation to obtain the physical matrix elements – is as follows. The first of these tasks is perfectly parallel, meaning that on a multiprocessor machine different elementary integrals can be evaluated simultaneously on different processors with effectively zero parallel overhead. Although the second step – transformation of integrals stored in the microprocessors – involves communication and synchronization overheads, it can be formulated in terms of multiplication of large, distributed matrices, a highly efficient procedure on parallel computers. With these scalable algorithms we routinely achieve aggregate performance in the tens of gigaflops range. This capability, which to our knowledge is unmatched, has allowed us to carry out sophisticated first-principles calculations of electron collisions with species such as N_2, CO, NO, H_2O, OH, and CO_2.

Highlights of these application include

• In a joint effort with the experimental group of Professor H. Ehrhardt of Kaiserslautern University in Germany, we have completed a comprehensive study of the cross sections for electron-impact excitation of the low-lying excited states of CO from threshold to about 4 eV above threshold. These studies should provide the most reliable estimates of the cross sections for excitation of CO in the technically important, but experimentally challenging, near-threshold region. The availability of both measured and calculated differential and integral cross sections offer a unique opportunity for an in-depth comparison of the measured and calculated cross sections. Cross sections were also calculated for impact energies well beyond the threshold region.

• We have also carried out a combined computational – experimental study of the cross section for electron-impact excitation at the low-lying excited states of N_2. Differential and integral cross sections were calculated for excitation of seven low-lying states (A $^3\Sigma_u^+$, B $^3\Pi_g$, W $^3\Delta_u$, a $^1\pi_g$, w $^1\Delta_u$, a' $^1\Sigma_u^-$, and B' $^3\Sigma_u^-$). Critical comparisons of these calculated cross sections with recent measurements by S. Trajmar of the Jet Propulsion Laboratory were also carried out for the A $^3\Sigma_u^+$, B $^3\Pi_g$, W $^3\Delta_u$, and a $^1\Pi_g$ states. These studies have provided the first robust values of the cross sections for excitation of the metastable A $^3\Sigma_u^+$ state of N_2 at near-threshold electron impact energies.

• We have studied the cross sections for near-threshold excitation of the lowest-lying excited state of OH by low-energy electrons. OH fragments are produced in flows of interest via dissociation of water vapor. No measured data are available for these cross sections.

• Cross sections for electron-impact excitation of H_2O to low-lying excited electronic states, which subsequently fragment to H and OH, were calculated.

References

1. K. Takatsuka and V. McKoy, Phys. Rev. A **30**, 1734 (1994)
2. C. Winstead, P.G. Hipes, M.A.P. Lima, J. Chem. Phys. **94**, 5455 (1991)
3. C. Winstead and V. McKoy, Adv. At. Mol. Opt. Phys. **36**, 183 (1996)

III. *The results of this research appear in the following publications.*

1. Collisions of Low-Energy Electrons with CO_2
   C.-H. Lee, C. Winstead, and V. McKoy
   J. Chem. Phys. **111**, 5056 (1999)
2. Absolute Differential Cross Sections for Electron-Impact Excitation of CO Near Threshold
   J. Zobel, U. Mayer, K. Jung, H. Ehrhardt, H. Pritchard, C. Winstead and V. McKoy
   J. Phys. B. **29**, 839 (1996)
3. Electron Collisions with Nitrous Oxide
   C. Winstead and V. McKoy
   Phys. Rev. A **57**, 3589 (1998)
4. Electron-NO Collisions
   F.J. Paixao, M.A.P. Lima, and V. McKoy
   Phys. Rev. A **53**, 1407 (1996)
5. Highly Parallel Computational Techniques for Electron-Molecule Collisions
   C. Winstead and V. McKoy
   Advances in Atomic, Molecular, and Optical
   Physics **36**, 183 (1996)
6. Electron Scattering by Small Molecules
   C. Winstead and V. McKoy
   Advances in Chemical Physics **96**, 103 (1996)

7. Parallel Computation of Electron-Molecule Collisions
   C. Winstead, H. Pritchard, and V. McKoy
   Computational Science and Engineering **2**, 34 (1995)

8. Electron Scattering by Water Molecules
   L.E. Machado, M.-T. Lee, L.M. Brescansin, M.A.P. Lima and V. McKoy
   J. Phys. B **28** 467 (1995)

9. Studies of Electron-Molecule Collisions on Massively Parallel Computers
   C. Winstead and V. McKoy
   Modern Electronic Structure Theory (World Scientific, 1995)

10. Electronic Excitation of CH_4 by Low-Energy Electron Impact
    C. Winstead, Q. Sun, V. McKoy, J.L.S. Lima, and M.A.P. Lima
    J. Chem. Phys. **98**, 2130 (1993)

11. Electron-Impact Excitation of [1.1.1] Propellane
    C. Winstead, Q. Sun, and V. McKoy
    J. Chem. Phys. **97**, 9483 (1992)

12. Electronic Excitation of Carbon Monoxide by Low-Energy Electron Impact
    Q. Sun, C. Winstead, and V. McKoy
    Phys. Rev. A1, **46**, 6987 46 (1992)

13. Low-Energy Electron Scattering by C_3H_6 Isomers
    C. Winstead, Q. Sun, and V. McKoy
    J. Chem. Phys. **96**, 4246 (1992)

14. Studies of Electron Collisions with Polyatomic Molecules Using Distributed-Memory Computers
    C. Winstead, P.G. Hipes, M.A.P. Lima, and V. McKoy
    J. Chem. Phys. **94** 5455 (1991)

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